the analyte [mouse IgG] to be trapped by the trapping substance [anti-mouse IgG F(ab')2 antibody] [see FIG. **30**B].

[0303] After washing the working electrode substrate with TBS-T, the solution containing 1 mg/mL of the labeled antibody obtained in Comparative example 2-1 was added to TBS-T containing 1% by mass of BSA so that the concentration of the labeled antibody was 20 μg/mL. 30 μL of the obtained mixture was poured into the above space. Thereafter, the analyte on the working electrode was labeled by incubating the working electrode substrate at 25° C. for 1 hour [see FIG. **30**B] (Test No. 7).

[0304] On the other hand, the control experiment when no analyte was present in Comparative example 2-2 was performed as follows. First, the working electrode substrate by which the analyte was not trapped was washed with TBS-T. Then, the solution containing 2 mg/mL of the labeled antibody obtained in Comparative example 2-1 was added to TBS-T containing 1% by mass of BSA so that the concentration of the labeled antibody was 20 μg/mL. 30 μL of the obtained mixture was poured into the above space. Thereafter, the working electrode substrate was incubated at 25° C. for 1 hour (Test No. 8).

(3) Measurement of Photocurrent

[0305] Silicone rubber was placed around the working electrode substrates of Test Nos. 5 to 8 so that a 0.2-mm-thick side wall was formed. Then, the space surrounded by the working electrode substrate and the silicone rubber was filled with the electrolytic solution obtained in Preparation example 2-3. Thereafter, the space filled with the electrolytic solution was sealed with the counter electrode substrate obtained in Preparation example 2-4 from the upper side of the working electrode substrate. Thus, the working electrode and the counter electrode are brought into contact with the electrolytic solution. Then, the detection chip including the working electrode substrate and the counter electrode was placed in an electrochemical measurement device. The working electrode lead and the counter electrode lead were connected to the ammeter.

[0306] The light source (wavelength: 781 nm, laser light source with an output power of 13 mW) emits excitation light from the working electrode substrate side toward the counter electrode substrate. Alexa Fluor750, i.e., a labeling substance [see **433** in FIG. **29**D] is excited by light radiation and electrons are generated. When the generated electrons are transported to the working electrode, current flows between the working electrode and the counter electrode. Then, the electric current was measured.

[0307] FIG. **31**A shows an outline explanatory view showing the detection process of the method for electrochemically detecting an analyte of Test No. 5 in Example 2-2. FIG. **31**B shows an outline explanatory view showing the detection process of the method for electrochemically detecting an analyte of Test No. 7 in Example 2. FIG. **32** shows examined results of a relationship between the kind of the detection method and photocurrent in Test example 2-2.

[0308] In the method for electrochemically detecting an analyte of Test No. 5, as shown in FIG. **31**A, the biotin labeled anti-mouse IgG antibody as the first conjugate [see **431***a* in the drawing], streptoavidin as the second conjugate [see **430***b* in the drawing], and the biotinylated AlexaFluor750-labeled DNA as the labeled form [see **430***c* in the drawing] are used. Here, the molecular weight of streptoavidin is about 53 kDa. Taking into consideration a steric hindrance when biotin of the biotin labeled anti-mouse IgG antibody is bound to streptoavidin, the number of AlexaFluor750 which can be bound to the biotin labeled anti-mouse IgG antibody of a molecule (molecular weight: about 150 kDa) is considered to be up to about four molecules. Further, the biotinylated AlexaFluor750-labeled DNA can be bound to three sites of four biotin-binding sites in the streptoavidin. Therefore, as shown in FIG. **31**A, photocurrents are generated from 9 to 12 labeling substances per molecule of antibody by the irradiation of the excitation light in the detection process. On the other hand, in the method for electrochemically detecting an analyte of Test No. 7, the labeled antibody [see **441** in FIG. **31**B] is used. Thus, as shown in FIG. **31**B, photocurrents are generated from 10 labeling substances [AlexaFluor750, see **443** in FIG. **31**B] per molecule of antibody [see **442** in FIG. **31**B] by the irradiation of the excitation light in the detection process. Therefore, unless taking into consideration DNA, it may be predicted that the photocurrent detected by the method for electrochemically detecting an analyte of Test No. 5 is the same as that detected by the method for electrochemically detecting an analyte of Test No. 7.

[0309] However, from the results shown in FIG. **32**, it is found that the photocurrent detected by the method for electrochemically detecting an analyte of Test No. 5 is 12 nA, while the photocurrent detected by the method for electrochemically detecting an analyte of Test No. 7 is 4.5 nA. From these results, it is found that, unexpectedly, the photocurrent detected by the method for electrochemically detecting an analyte of Test No. 5 is far larger than that detected by the method for electrochemically detecting an analyte of Test No. 7. Therefore, it is considered that a difference between the photocurrent detected by the method for electrochemically detecting an analyte of Test No. 5 and the photocurrent detected by the method for electrochemically detecting an analyte of Test No. 7 is dependent on the presence of DNA between the labeling substance and the binding substance.

[0310] A DNA exhibits hydrophilicity. Therefore, it is considered that the DNA has an interaction (hydrophilic interaction) with the working electrode body into which an electrolytic solution containing an aprotic solvent and a hydrophilic triethylene glycol (TEG) chain are introduced. On the other hand, when the electrolytic solution contains a protic solvent and a hydrophobic functional group is introduced into the working electrode body, it is considered that the interaction (hydrophobic interaction) is generated by using a substance having hydrophobicity in place of DNA.

[0311] The above results suggest that the analyte can be detected with high sensitivity by using the label binding substance in which the labeling substance is at least immobilized on the binding substance via the modulator which generates an interaction with the electrolytic solution and the working electrode site except the site bound to the trapping substance in order to label the analyte.

Preparation Example 2-5

[0312] Biotinylated-DNA and Alexa Fluor 750-labeled DNA were added to 1M sodium chloride-containing phosphate buffer so that their concentrations were 1 μM and 10 μM, respectively. The obtained mixture was heated at 80° C. for 1 minute. Thereafter, the mixture was cooled to 4° C. while decreasing the temperature of the mixture concerned to 1° C./min. Thus, the biotinylated-DNA was hybridized with the Alexa Fluor 750-labeled DNA to produce a biotinylated-DNA/Alexa Fluor 750-labeled DNA complex (see **370** in